

FLASH HYDROGENATION OF LIGNITE AND BITUMINOUS COAL IN AN ENTRAINED FLOW REACTOR

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Introduction

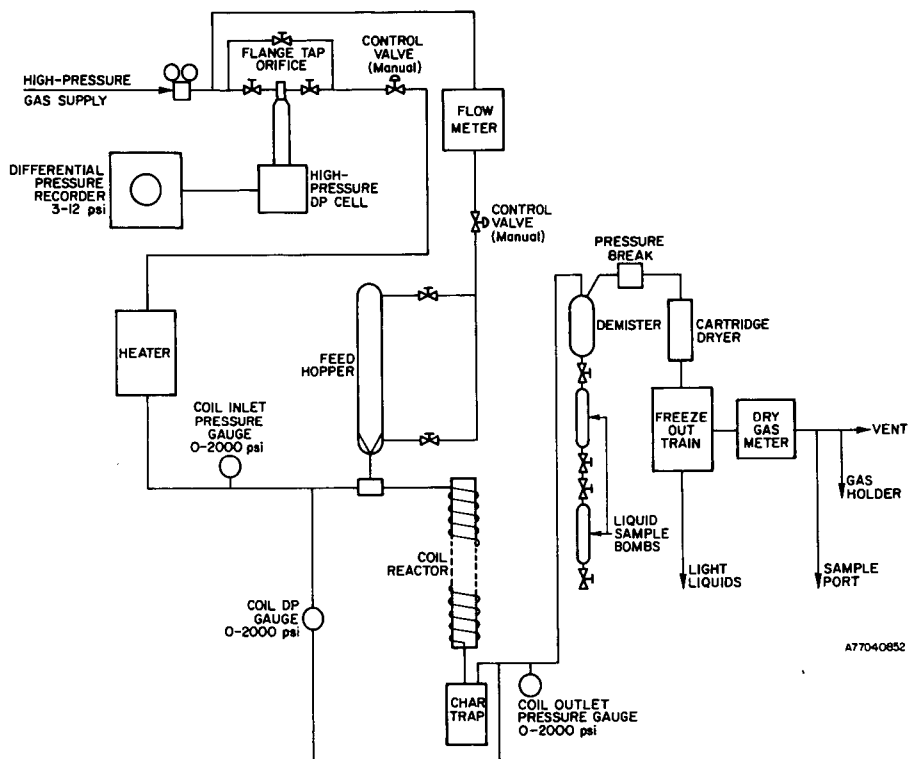
This paper is a report of some recent developments in an on-going investigation of short residence time hydrogenolysis of lignite and coal to produce fuel gases, ethane, gasoline blending stock constituents, fuel oil and spent char. The program has been underway for three years, and in addition to the bench-scale unit described here will include the construction and operation of a process development unit. In results obtained to date, both lignite and bituminous coal have been successfully processed in the bench-scale unit. In a typical run, approximately 50% of the feed carbon is converted to liquid and gaseous products; as much as 15% of the feed carbon has been found to report to the hydrocarbon liquid products, and 35% to carbon oxides, methane, ethane and minor amounts of propane and propylene. Heavy tars are not produced, allowing the spent char to be collected as a dry, free-flowing material. Approximately 50% of the feed carbon remaining in the spent char would be utilized in hydrogen production, and would be sufficient for a "balanced plant" operation.

Hiteshue, et al. (1) observed that when coal is heated rapidly in the presence of hydrogen at high pressure, high yields of gaseous and liquid products are obtained. Over the past several years, several development programs (2,3,4,5,6) have been implemented to explore the various aspects of rapid or "flash" hydropyrolysis in the light of eventual commercialization. The work described here is intended, in general, to complement the work of other investigators, and also elucidate the behavior of reactants and products during the course of the pyrolysis. The exploration of processing conditions appropriate for the recovery of maximum possible yields of liquids suitable for use as motor fuels is an important additional aspect of the IGT program. Johnson (4) postulated that the hydrocarbon liquids are released early in the pyrolysis, and are hydrogenated to methane and ethane in subsequent reaction steps.

In the work described here, our data show that in addition to relatively slow hydrogasification to methane and ethane, there is considerable vapor phase dehydroxylation of oxygenated monoaromatics (phenols + cresols) and dealkylation of substituted benzenes which results in significant changes in the distribution of BTX and oxygenated aromatics in the gasoline boiling range fraction of the hydrocarbon liquid products. The dehydroxylation and dealkylation reactions appear to be dependent upon both hydrogen partial pressure and temperature in a manner analogous to the vapor phase dealkylation of toluene in the presence of hydrogen described by Silsby and Sawyer (7).

Equipment

A flow diagram showing the major equipment in the bench-scale unit used in the work described here is shown in Figure 1. In operation, solids charged to the feed hopper are metered into a carrier stream of hydrogen; the hydrogen and entrained solids are then heated concurrently in a 1/8-in I.D. helical tube reactor which is 70 feet in length. A predetermined "temperature profile" is imposed over the length of the reactor by means of 12 independently controlled radiant heaters. The effluent from



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Figure 1. BENCH-SCALE UNIT

the reactor passes into the char trap where the spent char is disentrained and collected; the char-free gases are further cooled to ambient temperature to condense liquid products which are collected in sample bombs. The cooled gases are then reduced to essentially ambient pressure, and passed through a dryer and methanol/dry ice freeze-out train to strip benzene and other condensable materials from the make gas. The stripped gases are then metered, sampled, and vented.

A power plant grind (75% minus 200 mesh) of North Dakota lignite was used as solids feed in the work described here. Although feed gases can be preheated prior to mixing with feed solids, both the feed hydrogen and feed lignite were introduced into the reactor at ambient temperature. Runs using preheated hydrogen have been made, but analysis of data has not been completed at this writing; the results of these runs will be reported at a future time.

Experimental

In the experimental program described here, the objective was to explore the effect of heating rate on the distribution of feed carbon among products. Two kinds of temperature profile (Figure 2) were used in operating the equipment. In the first type, a linear heating rate was imposed on the lower end of the coil reactor. Due to a "chimney" effect, the upper end of the coil was heated by convection from the lower section, and idled at approximately 700°F. Using this first type of temperature profile, the feed was heated to a maximum temperature of 1500°F and quenched, with no appreciable residence time at 1500°F. In the second type of temperature profile, the lower section of the reactor was operated isothermally at 1500°F, and a linear heating rate imposed on the upper section of the coiled tube reactor, so that the reactants were held at 1500°F for times which were dependent upon the gas velocity chosen for a particular run.

Experimental Results

The operating conditions and results of the heating rate study are summarized in Table 1 which shows the distribution of carbon among products, the weight percent gasoline boiling range liquids obtained from the recovered liquids, and the weight percent of phenols + cresols and naphthalenes present in the gasoline boiling range liquids. Comparing Runs HR-1 and HR-3, it is apparent that with appreciable residence time at the maximum temperature (1500°F), feed carbon conversion actually decreased with increase in heating rate; a similar result was described by Johnson (4). At the higher heating rate, the liquid products were also more highly oxygenated, as measured by the amounts of phenols + cresols present in the gasoline boiling range liquids.

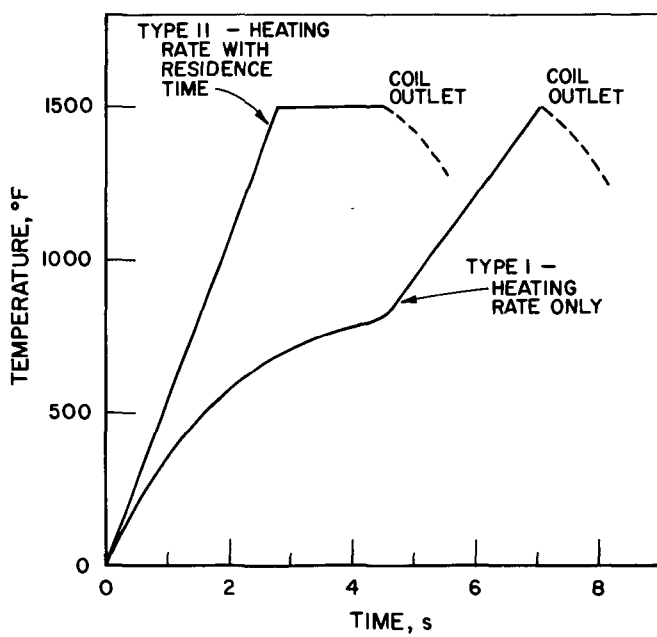
When a residence time at 1500°F was allowed, as in Runs HR-4 through HR-7, the methane yields improved considerably, and the degree of oxygenation of the liquid products as measured by the phenols + cresols in the gasoline boiling range liquids decreased. By inspection, however, there does not appear to be any effect that can be attributed to heating rate alone.

The intensity or severity of a time-temperature history can be measured by the magnitude of a severity function defined as -

$$\text{Severity Function} = \int_0^t k \, dt \quad 1)$$

where k is a reaction rate constant and t is time. Using published data for the hydrogasification of anthracene (8), the rate constant can be calculated from -

$$k = k_0 e^{-E/RT} \quad 2)$$



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Figure 2. TEMPERATURE PROFILES USED IN HEATING RATE STUDIES

where k is 9.0×10^5 and E is 30,700 Kcals per gram mole. For the non-isothermal time-temperature histories used here, the value of the severity function was obtained by dividing the length of the coil into increments and calculating an incremental severity at the average temperature of the section. The value of the severity function was then obtained from —

$$\text{Severity Function} = \sum_{i=1}^n k \Delta t_i \quad 3)$$

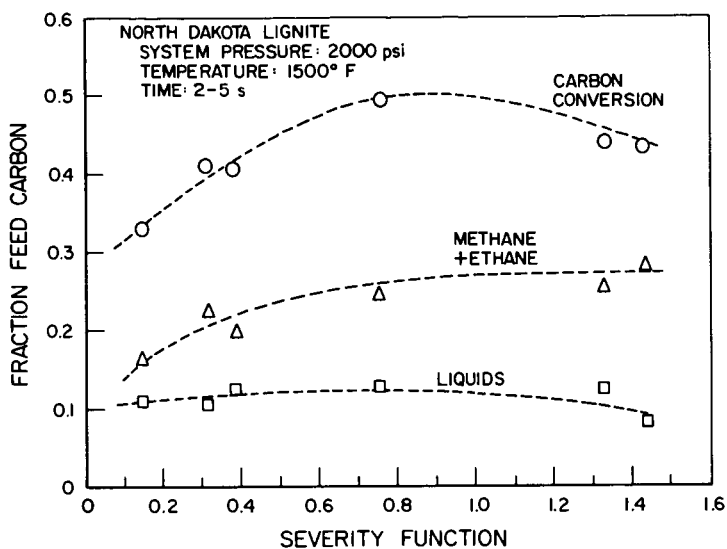
This severity function, based on anthracene hydrogasification kinetics is thus an arbitrary measure that can be used to characterize the thermal treatment under a given set of operating conditions. The data from the heating rate runs are plotted against severity function in Figure 3. From the figure, methane + ethane yield can be seen to increase with increase in severity function; while total carbon conversion passes through a maximum, suggesting that in a prolonged treatment, products are lost through thermal degradation. A similar result has been described by Steinberg, *et al.* (6). The total liquids yield also appears to decrease at high severity.

Table 1. OPERATING CONDITIONS AND SUMMARY OF RESULTS
OBTAINED IN HEATING RATE STUDIES WITH NORTH DAKOTA LIGNITE

Run No.	HR-2	HR-1	HR-3	HR-4	HR-5	HR-7	HR-6
Coil Outlet Pressure	2000	2000	2000	2000	2000	2000	2000
Coil Outlet Temperature	1500	1500	1500	1500	1500	1500	1500
Severity Function	0.383	0.315	9.148	0.767	1.346	1.434	1.954
Heating Rate, °F/s	125	152	348	412	155	1275	780
H ₂ /MAF Feed Weight Ratio	0.44	0.26	0.48	0.43	0.30	0.55	0.45
Carbon Distribution, %							
Liquids	12.25	11.03	11.71	13.19	12.44	8.59	7.30
Carbon Oxides	9.47	9.05	8.18	11.27	9.72	10.35	8.47
Methane	12.40	10.90	10.59	16.34	17.35	19.47	19.69
Ethane + Light Gas	7.37	11.36	6.26	8.43	8.33	8.63	8.61
Char	52.20	51.23	58.87	52.51	52.52	54.55	52.69
Gasoline Boiling Range Liquid, wt % total liquids	51.8	55.2	49.5	54.1	54.5	67.5	58.5
Phenols + Cresols in C ₅ -400°F Liquid	22.7	18.0	31.2	7.1	1.6	0.2	Tr
Naphthalene in C ₅ -400°F Liquid	12.6	15.2	10.8	6.7	5.3	15.2	7.8
	No Residence Time at 1500°F			Variable Residence Time at 1500°F			

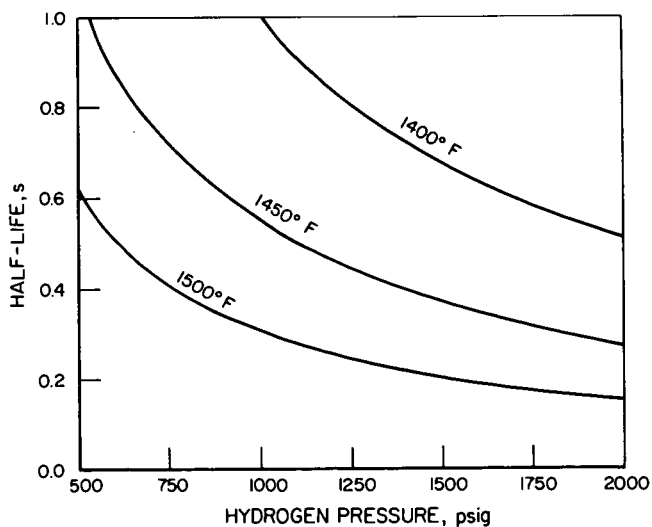
Discussion

Using kinetics published by Silsby and Sawyer (7), the change in the half-life of toluene with temperature and pressure was evaluated, and the results of these calculations are summarized in Figure 4. From the figure it can be seen that the dealkylation of toluene is accelerated by both an increase in temperature and hydrogen partial pressure. The observed changes in the composition of the gasoline boiling range liquids obtained from North Dakota lignite also appear to follow an analogous rule in which the dehydroxylation is accelerated by increase in hydrogen partial pressure (Figure 5). In a prior portion of the investigation, runs were made in the bench-scale unit at system pressures of 500, 1000, 1500, and 2000 psig, holding other parameters essentially constant. The fraction of phenols + cresols in the gasoline boiling range liquids was observed to decrease with increase in operating (essentially hydrogen) pressure while the fraction of BTX + ethylbenzene was observed to increase.



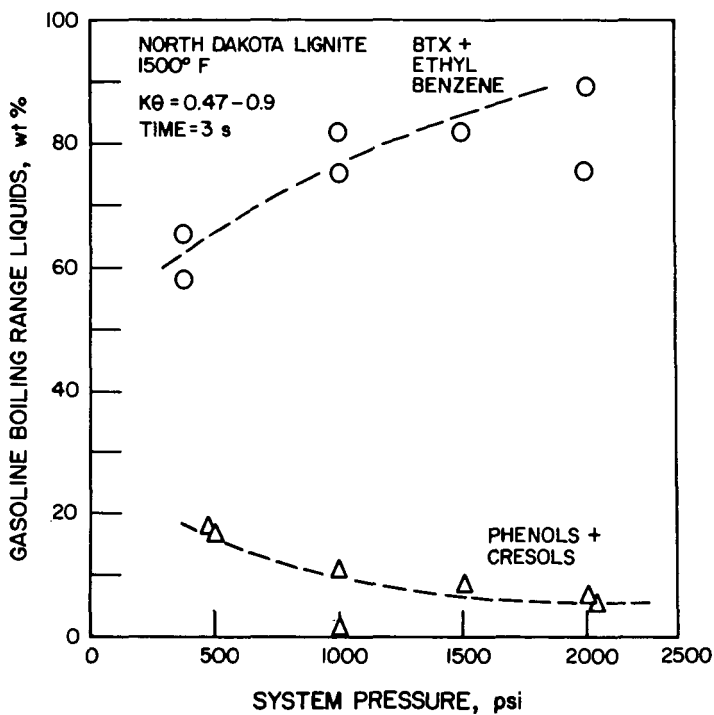
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Figure 3. CARBON CONVERSION, METHANE + ETHANE, AND LIQUIDS YIELDS IN HEATING RATE STUDIES



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Figure 4. CHANGE IN THE HALF-LIFE OF TOLUENE WITH TEMPERATURE AND HYDROGEN PARTIAL PRESSURE (6)



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Figure 5. CHANGE IN GASOLINE BOILING RANGE LIQUIDS COMPOSITION WITH PRESSURE

In the heating rate runs, the phenols + cresols fraction of the gasoline boiling range liquids was found to decrease with increase in severity function, as shown in Figure 6 with an attendant increase in BTX. The distribution of benzene, toluene, and xylene was observed to change as shown in Figure 7 which shows maxima for both toluene and xylene early in the pyrolysis with subsequent dealkylation to benzene. Finally, liquids, as they are devolved from the lignite at 1200° to 1300°F, are highly oxygenated, as shown in Table 2 which summarizes data from some runs with North Dakota lignite.

Table 2. OPERATING CONDITIONS AND SUMMARY OF RESULTS
OBTAINED AT 1200° AND 1300°F WITH NORTH DAKOTA LIGNITE

Run Number	PS-3	PS-5
Coil Outlet Pressure, psig	1500	1500
Coil Outlet Temperature, °F	1300	1200
Severity Function	0.334	0.217
H ₂ /MAF Feed Weight Ratio	0.31	0.53
Carbon Distribution, %		
Liquids	14.61	11.58
Carbon Oxides	9.46	9.23
Methane	9.62	5.88
Ethane + Light Gas	6.23	5.07
Char	64.51	68.33
Analysis of Gasoline Boiling Range Liquids		
BTX + Ethylbenzene	22.9	8.3
C ₉ Aromatics	5.4	4.0
Indenes + Indans	5.1	4.0
Phenols + Cresols	52.3	76.1
Naphthalenes	5.4	3.3
Not Identified	8.9	4.3
Total	100.0	100.0

Conclusions

From the foregoing it appears that the hydrocarbon liquids obtained from North Dakota lignite are highly oxygenated as they are devolved from the lignite, and are converted to BTX in the vapor phase by reaction with hydrogen. The conversion of oxygenated compounds to BTX exhibits a pressure and temperature dependency very similar to the dealkylation of toluene in the presence of hydrogen described by Silsby and Sawyer (7). The distribution of feed carbon among products and the composition of the gasoline boiling range liquids is a function of severity of thermal treatment, and appears to be independent of heating rate when heating rates of 150°F/s or higher are used.

The pressure dependency of the dehydroxylation reactions would affect reactor operations, particularly at low hydrogen-to-coal feed ratios where the hydrogen partial pressure would be substantially reduced with the release of methane, steam, and other reaction products. At this writing, the experimental work is being extended to the study of the effects of using preheated hydrogen. Analysis of data has not been completed, however, and the results of these runs will be reported at a future time.

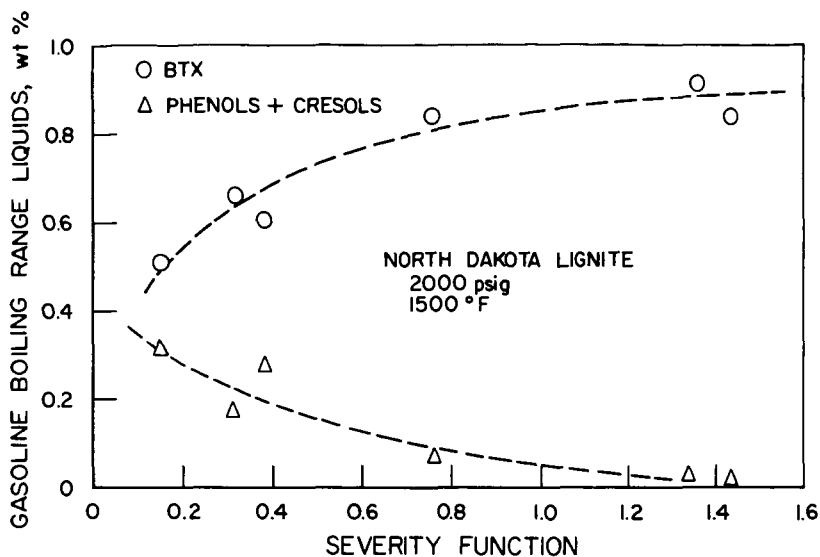


Figure 6. DISTRIBUTION OF BTX AND PHENOLS + CRESOLS WITH INCREASE IN SEVERITY

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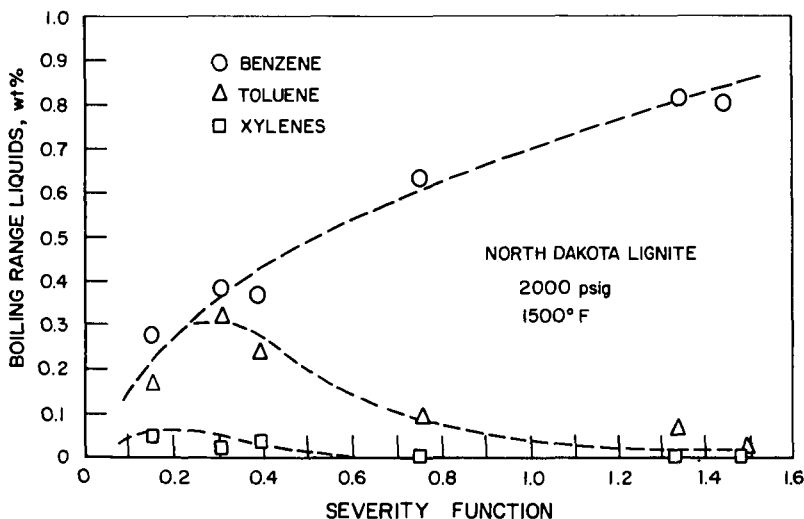


Figure 7. DISTRIBUTION OF BENZENE, TOLUENE, AND XYLENES IN THE BTX FRACTION OF GASOLINE BOILING RANGE LIQUIDS

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